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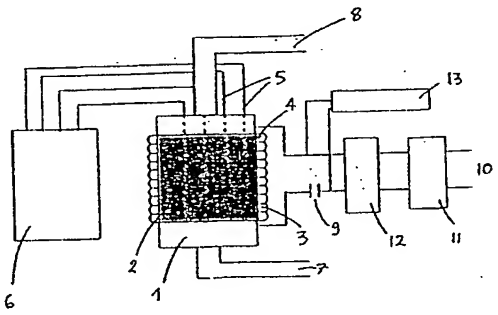
(54) **Process for the regeneration of a granular adsorbent, device for implementation, and composite.**

(57) Process for the regeneration of a granular adsorbent, characterized in that a container containing at least one granular adsorbent alone or in mixture is subjected to electromagnetic induction in a solenoid, device for implementation and composite comprising a granular adsorbent and susceptor.



The present invention relates to a process for the regeneration of a granular adsorbent and its device for implementation, by electromagnetic induction heating. It also relates to a granular carbon and graphite composite suitable for this process.

The use of activated carbon is considered as one of the most economical methods for treating water and air in order to eliminate a wide variety of pollutants. Its heterogeneous porous structure is suitable for eliminating most pollutants, although its capacity for absorbing a given pollutant is variable. It is particularly suitable for treating organic pollution responsible for unpleasant tastes and odours.

However, the service life of the carbon is limited by the saturation of the adsorption sites.

Its high production cost explains the existence of various regeneration processes. The standard processes are based on intermediate coolant fluid circulation through the carbon filter, resulting in the desorption of the adsorbate molecules. The fluid used is either overheated water vapour, or a hot gas.

The calorific energy provided by the fluid causes conduction heating of the materials of low thermal conductivity (approximately 0.15 $W.m^{-1}.°C^{-1}$ for carbon) which is detrimental to the thermal yield of the process.

Moreover, the fluid-adsorbent heat transfer gives rise to temperature gradients in the reactor in the flow direction of the fluid. Overheated zones exist which increases the likelihood of deterioration of the support, leading to premature ageing of the latter and chemical decomposition of the adsorbate.

The use of overheated water vapour involves the risk of decomposition of the adsorbate either by hydrolysis, or by chemical reaction. For example, the desorption of the chloroform by this process leads to a partial hydrolysis of the solvent and of its stabilizers with formation of hydrochloric acid, which is corrosive to pipes.

Moreover, the miscibility of the solvent with water requires an additional separation stage, such as distillation or liquid-liquid extraction, instead of simple decantation in the case of a biphase mixture.

The water vapour technique requires from 3 to 8 kg of vapour per 1 kg of recovered solvent, depending on the type of adsorbate and the size of the reactor.

The hot gas process is of limited economic interest due to the low thermal capacity of air and nitrogen (approximately 1 $kJ.kg^{-1}.°C^{-1}$), which is generally used, requiring the use of a large volume of purge gas leading to significant dilution of the desorbed product, for a high energy cost.

GB-A-1219819 describes a new regeneration design with the idea of creating in situ the heat necessary for desorption of the molecules fixed onto the carbon. For this purpose, the adsorbent placed between two electrodes is subjected to an electric current flow which leads to a heating of the material by Joule effect.

Numerous research projects have been carried out on this subject. EP-A-0104749 describes the operation of an installation for heating dispersed solid material by Joule effect.

However, the heterogeneous axial electrical resistance of the granular bed poses the problem of preferential passage of the current which creates a local heating of the reactor. Under these conditions, it is difficult to control the temperature during the operation. Moreover, the variation in temperature during the operation reduces the overall electrical resistance of the receiver, leading to a drop in heating efficiency. Numerous projects have been carried out on this subject aimed at improving the design and arrangement of the electrodes in the reactor (EP-A-0071675).

D. Mioduszewski (QED Corp, Ann. Arbor. 1982) was inspired by the idea of direct heating of the granular activated carbon to introduce a new process, without electrical contact: electromagnetic induction.

The material is heated by Foucault currents induced by an alternating magnetic field passing through this material. For this purpose, the filter, for example of carbon, is placed in the centre of a solenoid, through which a high-frequency current passes.

The work of Mioduszewski has shown the influence of the current frequency, power, diameter of the inductor, use of susceptors (i.e. granular materials which are good conductors of electricity), and nature of the adsorbate and the adsorbent on the heating kinetics within a frequency range between 4 and 6 MHz. Graphite grains have been tested as susceptors, but the influence of their grain size has not been studied.

However, the disadvantages linked to the use of this frequency range (formation of electric arcs, high thermal stress) compromise the prospect of desorbed product recycling.

A Japanese team has also worked on this subject (JP-A-57-150434).

US-A-4322394 describes a process utilizing microwave heating. The microwave range covers the frequency range between 5 MHz and 300 GHz.

This heating technique is characterized by a high power density but has a high economic cost.

JP-A-52-66896 presents an example of regeneration of activated carbon heated to a frequency range between 1 and 5000 MHz. An activated coconut shell carbon saturated with vinyl chloride is introduced into a microwave oven for one minute under reduced pressure (300mm Hg).

However, this technology involves the risk of forming an electric arc between the grains, which can cause the grain surface to deteriorate, leading to a wearing of the material and decomposition of the product desorbed.

Finally, EP-A-0460244 provides an overall view of the different electrical processes used for the regeneration of activated carbon.

In recent years, the prospect of recycling volatile organic compounds (VOCs) has brought new requirements with respect to regeneration quality.

In fact, such a process must be sure not to alter the physico-chemical properties of the adsorbate, nor those of the adsorbent.

It would therefore be desirable to have a process which can be used industrially, allowing the regeneration of adsorbents such as granular activated

carbon, saturated with volatile organic compounds which can then be recycled, thus making the process profitable, allowing the use of equipment widely available on the market (high-frequency generator with a frequency of less than 500 kHz, even in the case of small installations. Such a procedure should have useful thermal and economic balances, and if possible allow the selective desorption of the adsorbed compounds.

A subject of the present Application is therefore a process for the regeneration of a granular adsorbent, characterized in that a container containing at least one granular adsorbent alone or in mixture is subjected to electromagnetic induction in a solenoid.

The adsorbent can be for example a direct or indirect adsorbent such as zeolites, macrocrosslinked polymers such as acrylic esters, styrene-divinyl benzene, grafted silicas, clays, natural polymers such as chitosans, optionally grafted, chitin, plastic films treated to make them adsorbent, and preferably a granulated activated carbon. The latter can originate, for example, from wood, but preferably from fruit husks, in particular coconut shells.

The adsorbent can be presented in the form of flakes or shavings, but advantageously in the form of spheres or pellets. The preferred shape is that approximating to a sphere.

The average size or average diameter of the grains placed in the container is preferably approximately 3 mm, i.e. approximately 2 to 4 mm, preferably without exceeding the range of approximately 0.3 to 6 mm.

The electric resistivity of the product placed in the container is preferably less than 10^{-1} Ω.m, advantageously 10^{-2} Ω/m and in particular less than 10^{-3} Ω.m.

In the case of an adsorbent having poor resistivity, for example above 1 Ω.m, a susceptor, i.e. an element with very low resistivity, is added to the latter in order to compensate for this poor resistivity. The susceptor can represent for example from 5 to 50% of the mixture, and for example of the order of 15%. For example, strips or beads of steel can be used, and preferably beads of graphite. The susceptor is

presented preferably in the same form, or in a form approximating to the form of the adsorbent particles.

The adsorbent can be homogenous, or mixed with a second or other additional adsorbents, and optionally one or more susceptors.

The container can assume any suitable form, but the standard forms for such equipment, in particular cylindrical, are preferred.

The solenoid windings are preferably as close as possible to the adsorbent particles. They are therefore advantageously placed directly over the container containing the adsorbent. This container is preferably made from stainless steel or any other metal not heated by induction, such as steel, which allows homogeneous regeneration.

Preferably, all the adsorbent is subjected to the electromagnetic field.

An installation according to the invention can be very large; for example, an induced cylinder from 50 cm to 2 m in diameter and from 3 to 10 m in length can be produced. On the other hand, serious problems are encountered in the techniques of the prior art when large installations are to be produced.

The current passing through the solenoid should have the highest frequency possible. The frequency is advantageously greater than 20 kHz, in particular between 100 and 300 kHz and preferably about the latter value.

The nominal power of a high-frequency current generator is a function of its frequency. As a general rule, an increase in the useful power tends to reduce the working frequency.

A temperature of the adsorbent of the order of 100 to 220°C, preferably 120 to 200°C, is obtained by regulating the latter in order not to destroy the product adsorbed by the receiver. A thermocouple probe for example makes it possible to verify this parameter.

A subject of the present Application is also a device designed for the implementation of the process described above, characterized in that it comprises a container, preferably cylindrical, produced in particular [from] stainless steel,

surrounded by a solenoid linked to a generator of current with a frequency above 20 kHz, the said solenoid being advantageously equipped with a system for reducing temperature such as a water or air, optionally refrigerated.

As has been seen previously, the form of the container must be adapted to that of the solenoid. The container advantageously has an adsorbent capacity of more than a litre and preferably more than 100, even 1,000 litres.

A particular subject of the present Application is an above device, the container of which contains at least one granular adsorbent defined above and below. Other preferential devices have characteristics resulting directly from the preferred conditions for implementation of the process described above.

The present invention is put to remarkable uses in the regeneration of at least partially saturated adsorbents, in particular activated carbons in all their forms, such as grains, powders (grains of the order of approximately 300 µm), fibres (in particular in the form of agglomerates with an average size of 1 mm, for example from 0.5 to 4 mm, optionally mixed with at least one susceptor such as graphite, steel or copper in granular form.

This regeneration can be carried out in situ, at the adsorption site.

This regeneration is homogeneous, and has a useful thermal balance.

When using chlorinated solvents, it makes it possible to avoid the corrosion produced by hydrochloric acid during the regeneration using overheated water vapour.

The process which is the subject of the present Application makes it possible to regulate the temperature of the adsorbent, and in particular makes it possible to produce a temperature gradient and also to recover, even selectively, the different products adsorbed.

Nor does it give rise to pollutant emissions, and is implemented using a simple installation, with reduced management requirements.

By allowing recycling of both the adsorbate and the adsorbent, it preserves the service life of the latter.

The adsorbed products can originate from the treatment of gas or liquids, in particular volatile products, such as halogenated solvents, the halogen of which is bromine, fluorine or chlorine, sulphurated solvents such as dimethyl sulphoxide, dimethyl disulphide, oxygenated solvents such as the ketones such as acetone, alcanols such as methanol or ethanol, aromatic solvents such as benzene or toluene; generally also odoriferous molecules such as nitrogenated compounds such as methyl- or dimethylamine, sulphurated products such as sulphides, polysulphides or mercaptans, oxygenated products such as organic aldehydes or acids, aliphatic or aromatic hydrocarbides, vapours of fuels such as gasoline for cars.

Finally, a subject of the present Application is a composite characterized in that it comprises an adsorbent, preferably activated carbon and a susceptor, in particular formed from graphite grains, advantageously in more or less homogeneous mixture, the average grain size of which is in particular between 0.4 and 4 mm and the overall resistivity of which is below 10^{-2} Ω.m, as well as installations described above, the container of which contains such composites.

Figure 1 diagrammatically represents a laboratory assembly of a device allowing the implementation of the present process.

Figure 2 diagrammatically represents a device allowing continuous operation.

Figure 1 shows a container 1, filled with granular adsorbent 2, surrounded by a solenoid 3 cooled by pipes 4, allowing the circulation of a coolant liquid; four thermocouples 5 probe the temperature of the adsorbent and are linked to a data acquisition centre 6. The container 1 is provided with an inlet 7 and an outlet 8 of fluid to be filtered on the adsorbent.

The solenoid can for example have 6 or 9 windings according to the desired inductance, and is linked to one or more condensers 9 in order to adjust the frequency of the electromagnetic circuit; its diameter here is 14 cm and its height 18 cm.

In this assembly the current originates from the network 10 and is modified by a rectifier and an inverter, and comprises an oscilloscope for controlling its parameters.

Figure 2 schematically shows two adsorbent filters installed in parallel, operating simultaneously, one adsorbing, the other desorbing, in order to allow continuous operation of the process.

The induction heating leads to desorption in two stages; the water present in the internal structure of the material is first released and eliminated at the level of the separator, then the solvent, as well as some traces of water contained in the microporous structure of the carbon are vaporized.

These desorbed solvent vapours pass through a condenser 13. The solvent, in liquid form, is then passed into the separator 14, in order to eliminate the residual water by simple decantation.

The recovered solvent 15 is then recycled after optional addition of a stabilizer.

The following examples illustrate the present invention, without however limiting it.

Example 1: Regeneration of activated carbon (frequency 263 kHz)

An adsorbent, constituted by 635 g of coconut shell carbon (NC 60 median diameter 3.8 mm) is introduced into a glass reactor with an internal diameter of 120 mm and height of 300 mm.

The NC 60 carbon is charged with dichloromethane vapour (170 g). This operation is carried out by purging with air having a solvent concentration of 50 $g.m^{-3}$ and passing over the column at a rate of 63 $m.h^{-1}$ (flow rate = 11.9 $1.mn^{-1}$) for 5 hours 40 minutes.

The influent and effluent concentrations are checked by gas phase chromatography with a flame ionization detector.

After this adsorption operation, the activated carbon is heated by electromagnetic induction at a frequency of 263 kHz using a high-frequency current

generator with a triode. For this purpose, the carbon column is placed inside a copper solenoid, with double windings numbering six, with inductance of 2.9 µH, linked to the generator. The solenoid has a diameter of 14 cm and a height of 18 cm. This solenoid and the different electromechanical components (condensers, triode, power transformers) are cooled down with water with a flow rate of 400 $L.h^{-1}$. This cooling water circulates in a closed circuit at a temperature below 25°C. When this temperature is reached, the water is topped up from the mains in order to maintain good cooling efficiency.

First of all, the reactor is heated for 24 minutes in free convection, until a temperature of 140°C is reached, which corresponds to maximum desorption kinetics. The electric power involved is 2 kW. This is accompanied by an increase in pressure of saturating vapour of the solvent in the reactor which limits the desorption by the establishment of a new state of thermodynamic equilibrium favourable to adsorption.

Nitrogen purging is then introduced in order to reduce the pressure of the solvent vapour passing over the filter at a rate of 50 $m.h^{-1}$ for 30 minutes, while maintaining a constant temperature of 140°C in the reactor with a thermal regulation system.

The rate of regeneration of activated carbon obtained under these conditions is 90%.

Example 2: Regeneration of activated carbon (frequency 263 kHz) with susceptor.

A mixture, constituted by 635 g of NC 60 carbon (median diameter 3.8 mm) and 70.5 g of graphite (diameter 4 mm) is placed in the same reactor as that described in Example 1.

The NC 60 carbon is charged with dichloromethane vapour (170 g). The adsorption protocol is identical to that mentioned previously.

The activated carbon is heated by electromagnetic induction at a frequency of 263 kHz under a power of 1.8 kW.

The reactor is heated for 12 minutes with free convection until a temperature of 140°C is reached.

Nitrogen purging is then introduced for 30 minutes under the same conditions as in Example 1.

This experiment has made it possible to obtain a regeneration rate of 90%.

Example 3: Regeneration of activated carbon (frequency 140 kHz)

An adsorbent, constituted by 635 g of NC 60 carbon (median diameter 3.8 mm) is placed in the same reactor as that described in Example 1.

The NC 60 carbon is charged with dichloromethane vapour (170 g). The adsorption protocol is still identical to that described in Example 1.

The activated carbon is heated by electromagnetic induction at a frequency of 140 kHz under a power of 2 kW. The solenoid, of the same design as previously, is constituted by nine windings for an inductance of 6.5 µH.

The reactor is heated for 35 minutes with free convection until a temperature of 140°C is reached.

Nitrogen purging is then introduced for 30 minutes under the same conditions as in Example 1.

After 30 minutes, an activated carbon regeneration rate of 90% is also observed.

CLAIMS

1. Process for the regeneration of a granular adsorbent, characterized in that a container containing at least one granular adsorbent alone or in mixture is subjected to electromagnetic induction in a solenoid.

2. Process according to claim 1, characterized in that the granular adsorbent alone or the mixture has a resistivity of less than 10^{-1} Ω.m.

3. Process according to claims 1 to 2, characterized in that the frequency of the electric current passing through the solenoid in order to create the electromagnetic induction is greater than 20 kHz.

4. Process according to one of claims 1 to 3, characterized in that the granular adsorbent is mixed with a granular susceptor.

5. Process according to claim 4, characterized in that the susceptor grains have a size and shape approximating to that of the adsorbent.

6. Process according to one of claims 4 and 5, characterized in that the susceptor is graphite.

7. Process according to one of claims 1 to 6, characterized in that the solenoid comprises a cooling system.

8. Process according to one of claims 1 to 7, characterized in that the current passing through the solenoid is regulated in order that the average temperature of the adsorbent is approximately from 100 to 200°C.

9. Process according to one of claims 1 to 8, characterized in that the current is applied according to a gradient allowing the heating by successive stages of the adsorbent.

10. Device for implementation of the process according to claim 1, characterized in that it comprises a container surrounded by a solenoid linked to a generator of current with a frequency greater than 20 kHz.

11. Device according to claim 10, characterized in that the solenoid is equipped with a system for reducing its temperature.

12. Composite comprising a granular adsorbent and a granular susceptor, the average size of which is between 0.4 and 4 mm and the overall resistivity of which is below 10^{-2} Ω.m.

13. Composite according to claim 12, characterized in that the adsorbent is an activated carbon, and the susceptor is graphite.

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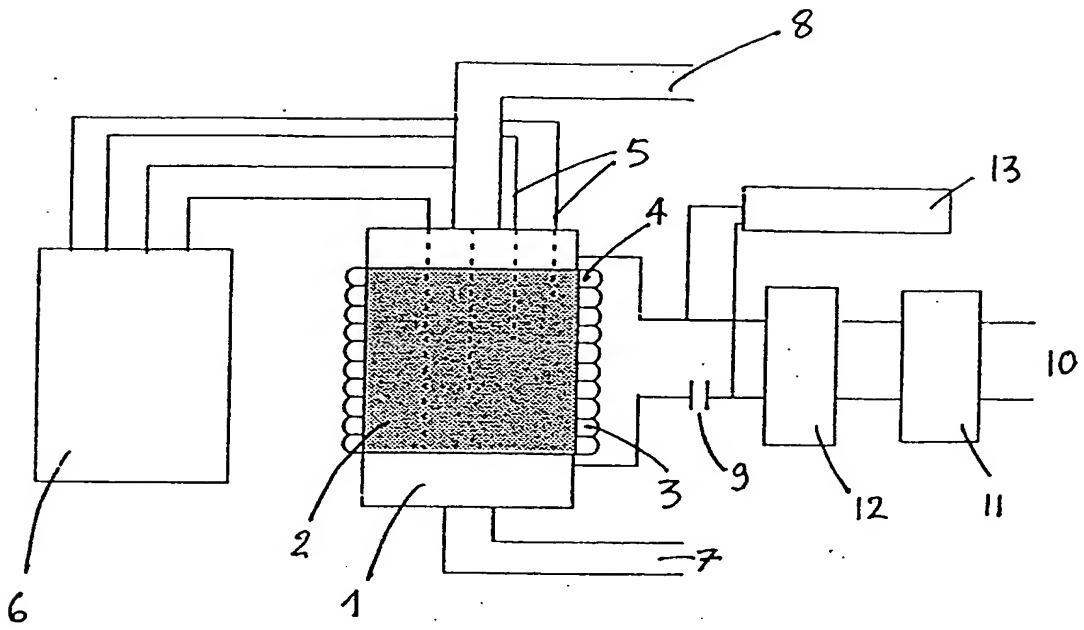

Figure 1

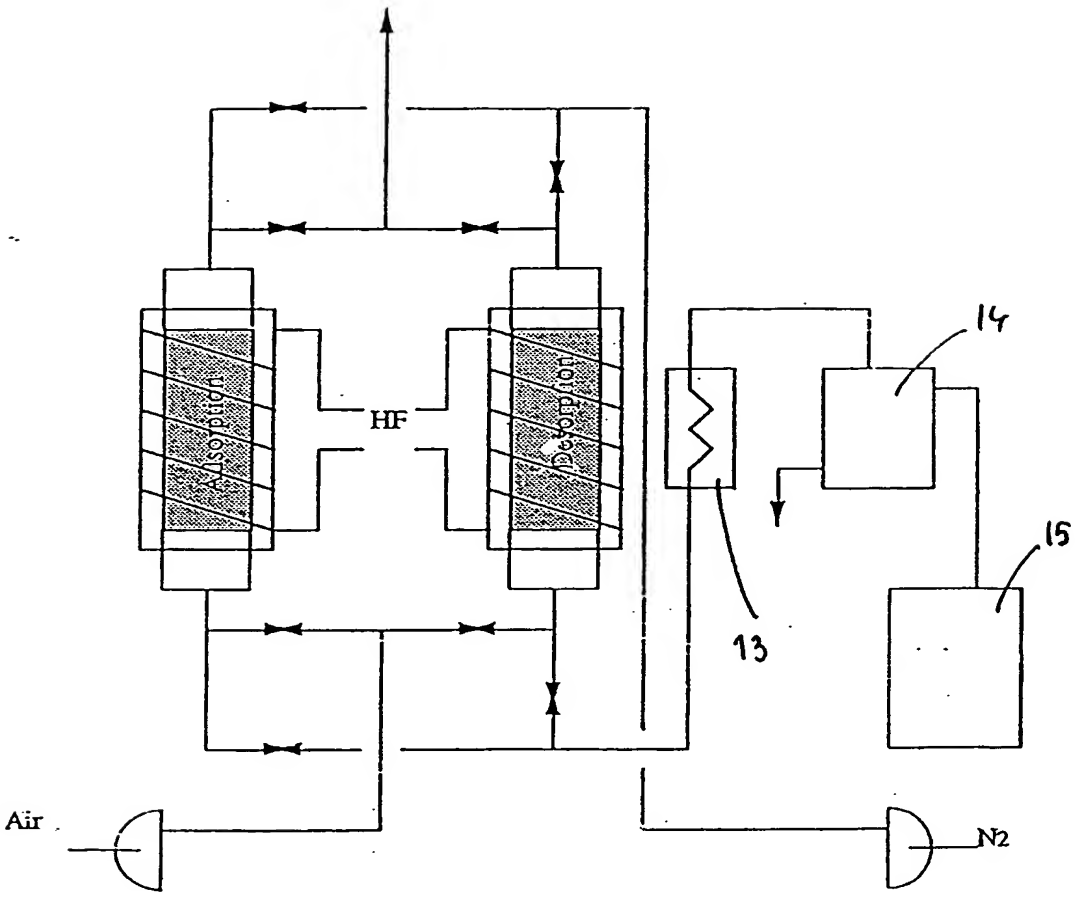

Figure 2